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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/CA94/00165 <b>(22) International Filing Date:</b> 22 March 1994 (22.03.94)  <b>(30) Priority Data:</b> 035,371 22 March 1993 (22.03.93) US 083,472 30 June 1993 (30.06.93) US  <b>(71) Applicant:</b> E.R.T. ENVIRONMENTAL RESEARCH TECHNOLOGY K.S.P.W. INC. [CA/CA]; Suite 100, 3429 Drummond Street, Montreal, Quebec H3G 1X6 (CA). <b>(72) Inventor:</b> KOZLOWSKI, Zdzislaw, Janusz; 4555 Bonavista Avenue, #405, Montreal, Quebec H3W 2C7 (CA). <b>(74) Agents:</b> WILKES, Robert, A. et al.; Shapiro Cohen Andrews Finlayson, Suite 2001, 112 Kent Street, P.O. Box 3440, Stn. D, Ottawa, Ontario K1P 6P1 (CA).		<b>(81) Designated States:</b> AU, BR, CA, CN, CZ, FI, JP, KP, KR, NO, NZ, PL, RO, RU, SD, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> WATER TREATMENT PROCESS  <b>(57) Abstract</b>  A process for recovering small amounts of liquid contaminants from water, which are present in the water either as solute or as the disperse phase of an emulsion. The process comprises contacting the contaminated water with an effective amount of a particulate polyurethane liquid sorbent, by mixing the sorbent and contaminated water together. The sorbent is removed from the water, typically by a simple filtration step. If required, the water can be treated more than once. The recovered contaminating liquid can be separated from the sorbent by a centrifugation step, and the sorbent re-used. In a typical case the hydrocarbon content of water containing 10 % of emulsified diesel fuel can be reduced to less than 200 ppm in a single treatment.		

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### WATER TREATMENT PROCESS

This invention relates to methods of removing relatively small amounts of substantially immiscible contaminants from water. In particular it is concerned with removing relatively small amounts of substantially immiscible contaminants from water in which the contaminant is either dissolved, or suspended as a more or less stable emulsion in which the contaminant is the disperse phase.

Although many organic compounds, especially liquids, are generally regarded as being insoluble in water. In fact this is only true in a macroscopic sense: many apparently insoluble or immiscible liquid organic compounds have a solubility in water of up to 1,000 ppm, and sometimes more. Further, many of these seemingly immiscible liquid compounds can be dispersed, at levels up to at least 100,000 ppm, that is 10%, in water as an emulsion having some stability and in which the immiscible liquid is the disperse phase. Typical examples are hydrocarbons. Oil and water appear to form two separate immiscible phases, and yet the solubility of hydrocarbons in water increases as the molecular weight decreases. It is also relatively easy to create unintentionally crude oil-water emulsions with significant stability: such emulsions are a major problem in cleaning ships tanks. It is also well known that removing such small amounts of a liquid contaminant from water is difficult, especially if the level of contaminant in the water after treatment is to be below 1.0 ppm.

In Canadian Application 2,085,951 is disclosed a new class of particulate liquid sorbents which are described therein as being particularly useful in cleaning up a wide range of spilled liquids. These liquid sorbents are primarily a particulate polyurethane product. One of the main advantages of these liquid sorbents is that separation of the absorbed liquid from them is relatively straight forward, requiring only a centrifugation step. A further advantage is that once the sorbed liquid has been removed in the centrifuge the particulate liquid

sorbent can be re-used. As described, the particulate liquid sorbent is used by spreading it onto the spilt liquid, a prime example being an oil slick on water. There is no suggestion in Canada 2,085,951 that these liquid sorbents will function at all when blended into a liquid system.

This invention seeks to extend the range of usefulness of these liquid sorbents by using them to remove from water small amounts of essentially immiscible contaminants that are present in the water in relatively small amounts either in solution, or as the disperse phase of an emulsion.

Thus in its broadest aspect this invention seeks to provide a process for recovering small amounts of liquid contaminants from water, which are present therein either as solute or as the disperse phase of an emulsion, which process comprises:

(a) contacting the contaminated water with an effective amount of particulate polyurethane liquid sorbent;

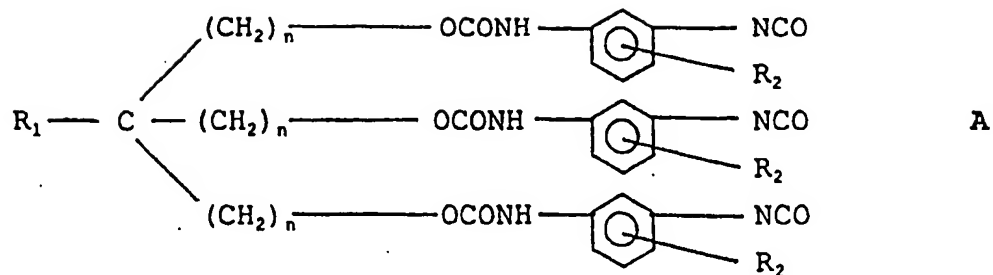
(b) maintaining the liquid sorbent in contact with the contaminated water for a time period sufficient to allow the liquid sorbent to sorb a significant amount of the liquid contaminant;

(c) separating the liquid sorbent containing liquid contaminant from the water by a filtration step; and if desired

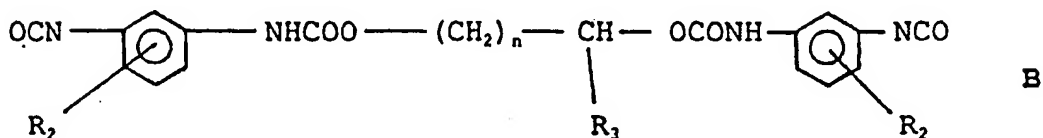
(d) separating the liquid contaminant from the liquid sorbent.

As is disclosed in Canada 2,085,951, the particulate solid liquid sorbent is readily separable from the absorbed liquid, and reusable. The solid sorbent comprises a particulate polyurethane liquid sorbent prepared by a process comprising :

(i) reacting together at a temperature of from 180° to 200°, for a time of less than 10 minutes, a prepolymer of the formula A:



with a prepolymer of the general formula B:



in the presence of a lower alkyl ester of the general formula C:



in which:  $n$  represents 1, 2, or 3;

$\text{R}_1$  represents a lower alkyl group having 1 to 6 carbon atoms;

$\text{R}_2$  represents hydrogen or a lower alkyl group having 1 to 4 carbon atoms; and

$\text{R}_3$  and  $\text{R}_4$  represent a lower alkyl group having 1 to 3 carbon atoms,

and when  $\text{R}_2$  is other than hydrogen, it is in the meta or para position relative to the  $-\text{NH}-$  linkage;

and wherein the weight ratio of prepolymer of formula A to prepolymer of formula B is about 3:1, and the reaction mixture contains from 22% to 25% by weight of ester solvent;

(ii) cooling the thus formed polymer;

(iii) adding thereto an alcoholic medium chosen from the group consisting of:

(a) ethanol; or

(b) a mixture of ethanol, methanol, and water containing 85% by weight ethanol, up to 15% by weight methanol, remainder to 100% water, or

(c) ethanol containing from 4% to 6% by weight isopropanol;

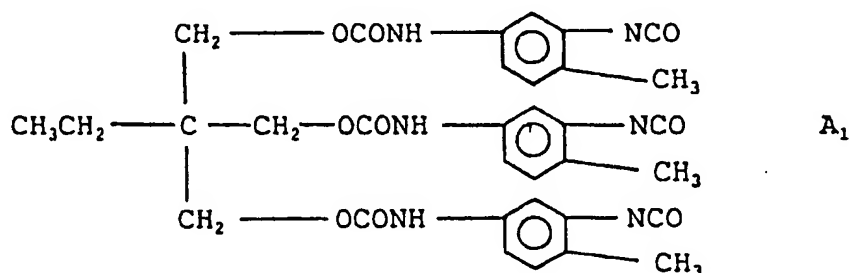
(iv) adding thereto with mixing hexamethylene tetramine,

(v) allowing the spontaneous reaction to proceed thereafter during which a temperature in the range of 55° to 65° is developed, and during which at least some of both the lower alkyl ester solvent, the alcoholic medium, and any water present, evaporate and

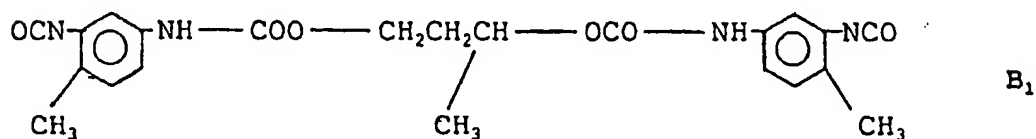
(vi) recovering the particulate polyurethane product.

Preferably, microspheres comprising an aluminosilicate shell containing gas having a diameter of from 10  $\mu\text{m}$  to 100  $\mu\text{m}$  are added to the reaction mixture between steps (iii) and (iv).

Preferably, (i) the prepolymer has the formula  $A_1$ :



(ii) the prepolymer B has the formula  $B_1$ :



and (iii) the lower alkyl ester solvent is ethyl acetate, and the alcoholic medium is ethanol.

These particulate liquid sorbents are more particularly described in Canadian Application 2,085,951. Hereafter, they will be referred to as RPA.

The process of this invention is straightforward. First, the contaminated water is contacted with an adequate amount of RPA. As the amount of contaminant in the water is low not very much RPA is required. It is relatively simple to ascertain how much will be adequate by way of some small scale tests. Alternatively, a constant amount of RPA can be used, even though in many cases this will be too much. For water systems containing up to at least 500 ppm of hydrocarbons, as both emulsion and solute, a ratio of 1.765 kg of RPA to 100 litres of contaminated water has been found to be satisfactory.

After contacting the contaminated water with RPA, it is necessary to allow an adequate contact time, so that the RPA can sorb the liquid contaminant. A time period of a few minutes has been found sufficient.

The RPA containing the liquid contaminant is then removed by a simple separation step, which itself also provides a part of the required contact time. A gravity filtration step, using a suitable paper or fabric filter operating at a flow rate of about 2 litres/min has been found to be satisfactory. When water containing significant amounts of contaminant is being treated rather than filtering all of the water, the liquid sorbent loaded with sorbed contaminant can be removed from the water by a porous net or other suitable means.

In an alternative arrangement, a mixing step as such can be avoided, by using a filter unit which comprises a plurality of layers of RPA in sequence. A convenient arrangement is to use a substantially conical filter, containing a plurality of separated layers of RPA. As the contaminated water flows slowly through the separate layers adequate contact time is readily achieved. With this arrangement, for example when using

1.675 kg RPA per 100 litres of contaminated water, three layers containing about 775 g, 500 g, and 400 g in sequence in a conical filter have been found to be effective. Each layer of RPA preferably is kept in its place by fabric layers both above and below it.

Although described above as essentially a batch process, this invention is not so limited, and can readily be operated continuously. Furthermore, it is also contemplated that it might be required to treat a given sample of contaminated water more than once to attain a desired residual level of contaminant.

In the following Table is shown the results of a sequence of ten test runs in which the amount of hydrocarbon was steadily reduced. At hydrocarbon levels above about 100 ppm at least some emulsion is present; at hydrocarbon levels below about 100 ppm substantially all of the hydrocarbon is dissolved.

Hydrocarbon Content.	
Before Test, % or ppm.	After Test, ppm.
10% (a)	1.2
5% (c)	135
2% (c)	75
420 (a)	11.0
315 (a)	16.0
200 (a)	7.1
130 (a)	7.8
60 (b)	1.2
55 (a)	135
38 (a)	2.6
29 (b)	0.8
6.7 (b)	2.4
1.4 (b)	0.6



Notes: Hydrocarbon used : (a) diesel fuel  
(b) gasoline  
(c) crude oil

In each of these tests, the amount of RPA was 1.675 kg/100 litres of contaminated water, and the filter flow rate was 2 litres/min. The very high oil content figures were assessed as these represent typical values obtained when cleaning ships oil tanks which have been ballasted with water.

As is explained in more detail in Canada 2,085,951, the liquid sorbent can be freed of sorbed liquid by a simple centrifugation step. It is preferred that the RPA be centrifuged to free it of sorbed contaminant liquid before being reused. It appears that the process is equally effective with either fresh RPA, reused RPA, or a mix of fresh and used RPA.

## CLAIMS:

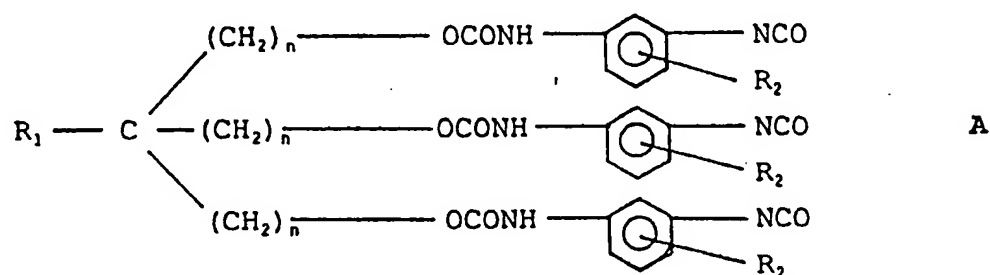
1. A process for recovering small amounts of liquid contaminants from water, which are present therein either as solute or as the disperse phase of an emulsion, which process comprises:

(a) contacting the contaminated water with an effective amount of particulate polyurethane liquid sorbent;

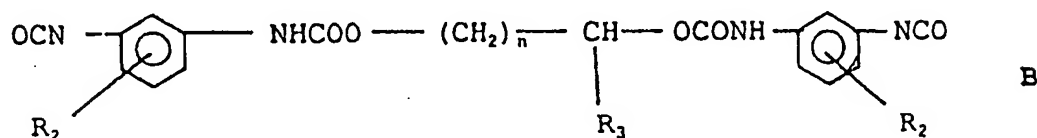
(b) maintaining the liquid sorbent in contact with the contaminated water for a time period sufficient to allow the liquid sorbent to sorb a significant amount of the liquid contaminant; and

(c) separating the liquid sorbent containing liquid contaminant from the water by a filtration step; wherein the solid sorbent comprises a particulate polyurethane liquid sorbent prepared by a process comprising :

(i) reacting together at a temperature of from 180° to 200°, for a time of less than 10 minutes, a prepolymer of the formula A:



with a prepolymer of the general formula B:



in the presence of a lower alkyl ester of the general formula C:



in which:  $n$  represents 1, 2, or 3;  
 $R_1$  represents a lower alkyl group having 1 to 6 carbon atoms;  
 $R_2$  represents hydrogen or a lower alkyl group having 1 to 4 carbon atoms;

and

$R_3$  and  $R_4$  represent a lower alkyl group having 1 to 3 carbon atoms,

and when  $R_2$  is other than hydrogen, it is in the meta or para position relative to the -NH- linkage;

and wherein the weight ratio of prepolymer of formula A to prepolymer of formula B is about 3:1, and the reaction mixture contains from 22% to 25% by weight of ester solvent;

(ii) cooling the thus formed polymer;

(iii) adding thereto an alcoholic medium chosen from the group consisting of:

(a) ethanol; or

(b) a mixture of ethanol, methanol, and water containing 85% by weight ethanol, up to 15% by weight methanol, remainder to 100% water, or

(c) ethanol containing from 4% to 6% by weight isopropanol;

(iv) adding thereto with mixing hexamethylene tetramine,

(v) allowing the spontaneous reaction to proceed thereafter during which a temperature in the range of 55° to 65° is developed, and during which at least some of both the lower alkyl ester solvent, the alcoholic medium, and any water present, evaporate and

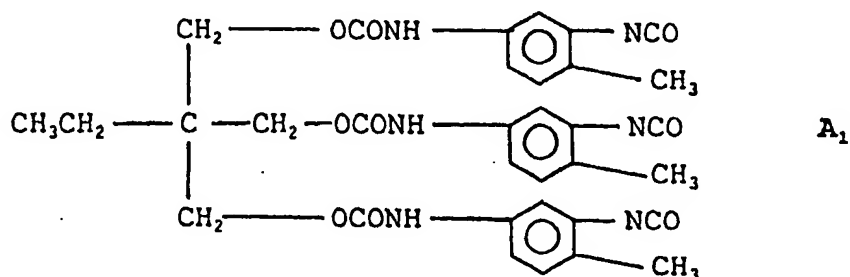
(vi) recovering the particulate polyurethane product.

2. A process according to Claim 1 further including:

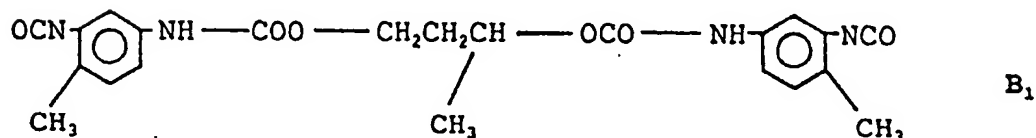
(d) separating the liquid contaminant from the liquid sorbent.

3. A process according to claim 1 wherein microspheres comprising an aluminosilicate shell containing gas having a diameter of from 10  $\mu\text{m}$  to 100  $\mu\text{m}$  are added to the reaction mixture between steps (iii) and (iv).

4. A process according to Claim 1 wherein  
(i) the prepolymer has the formula  $A_1$ :



(ii) the prepolymer B has the formula  $B_1$ ,



and (iii) the lower alkyl ester solvent is ethyl acetate, and the alcoholic medium is ethanol.

5. A process according to claim 1 wherein the contaminant is a liquid hydrocarbon.

6. A process according to claim 5 wherein the contaminant is a substantially dissolved liquid hydrocarbon.

7. A process according to claim 5 wherein the contaminant is a substantially emulsified liquid hydrocarbon.

8. A process according to Claim 1 wherein the contaminated water is contacted with the particulate liquid

sorbent by passing the water at a low flow rate through a plurality of beds of particulate sorbent in sequence.

9. A process according to Claim 1 wherein the water contains up to 1,000 ppm of dissolved contaminating liquid.

10. A process according to Claim 1 wherein the water contains up to 100,000 ppm of emulsified contaminating liquid.

11. A process according to Claim 1 wherein the contaminating liquid is hydrocarbon.

12. A process according to Claim 11 wherein the hydrocarbon is chosen from crude oil, oil, gasoline and diesel fuel.

## INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/CA 94/00165

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 5 B01D17/02 B01J20/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 B01D C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,1 526 159 (RAYMOND BOIS & SOCIÉTÉ SALPA) 24 May 1968 see the whole document ---	1,2,5-7, 11,12
A	EP,A,0 013 412 (BASF AG) 23 July 1980  see page 3, line 16 - page 14, line 31 ---	1,2,5-8, 11,12
P,A	WO,A,93 12878 (E.R.T. ENVIRONMENTAL RESEARCH TECHNOLOGY K.S.P.W. INC.) 8 July 1993 cited in the application see page 9; claims 1-3,5-8 -----	1-4



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

8 June 1994

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/CA 94/00165

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-1526159		BE-A- 712125 DE-A- 1767197 LU-A- 55665 NL-A- 6804659	15-07-68 29-04-71 15-07-68 11-10-68
EP-A-0013412	23-07-80	DE-A- 2901335 AT-T- 6625 CA-A- 1129783 US-A- 4279757	31-07-80 15-03-84 17-08-82 21-07-81
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